

The Effect of Sulfur Dioxide on the De-Novo-Synthesis of PCDD/PCDF on Fly Ash

L. Stieglitz, H. Vogg, H. Bautz, J. Beck, G. Zwick

Nuclear Research Center, P.O. Box 3640

7500 Karlsruhe FRG

ABSTRACT

The formation of PCDD/PCDF on fly ash was investigated in the presence of SO₂. No significant effect was found for standard fly ash. With modified fly ash a decrease of the PCDD/PCDF production was observed for 600 - 900 mg/m³ SO₂ in the absence of water vapor.

INTRODUCTION

The reaction of carbonaceous particulate matter with inorganic halides at 300 °C was recognized as an important pathway for the formation of polychlorinated dibenzodioxins and -furans [1,2]. In these reactions the role of copper (II) ions is of fundamental importance as a reagent to induce reactions in the presence of oxygen on the surface of particulate carbon, which lead on one side to the oxidation of carbon to CO₂ and on the other side to the chlorination of aromatic structures with the production of a variety of aromatic halogenated compounds such as chlorobenzenes, -biphenyls and naphthalenes [3]. These redox processes, especially the postulated conversion of chloride/HCl to chlorine by Cu²⁺, may be influenced by the presence of sulfur dioxide [4]. The influence of SO₂ in the gas phase on the PCDD/PCDF formation was studied as a contribution to a better understanding of these processes

EXPERIMENTAL

In the investigations two different samples were used: A) fly ash from a municipal waste incinerator, homogenized and ground; PCDD concentration 320 ng/g, PCDF concentration 395 ng/g; B) fly ash, annealed at 500 °C for 6 hrs to remove organic matter, then 4 % purified charcoal added (PCDF/PCDD concentration of mixture < 0,3 ng/g). The samples (1 g) were heated in a vertical quartz tube on a frit in an upward air stream (50 ml/min) at 300 °C for 2 hrs. The composition of the air stream was adjusted to contain independently different concentrations of sulfur dioxide (0/300/600/900 mg/m³), hydrogen chloride (0/300 mg/m³) and water vapor (0/100 g/m³). Further experimental and analytical details are described elsewhere [2,3].

RESULTS AND DISCUSSION

The results of the experiments with genuine fly ash (A) are presented in table 1. The data in the first three columns show the effect of SO₂ concentrations of 300 and 600 mg/m³ on the PCDD/PCDF formation at 300 °C in the presence of water vapor compared with an atmosphere without SO₂. Generally the concentrations formed are similar, there is a slight increase of the sum of PCDD from 1962 to 2299 ng/g, and of PCDF from 2112 to 3164 ng/g in the presence of 300 mg/m³ SO₂. By a further

Table 1: Effect of SO₂/HCl on the Formation of PCDD/PCDF on Fly Ash
Temperature 300 °C, 2 hrs.

Gasphase	SO ₂ mg/m ³	—	300	600	300	300
	HCl mg/m ³	—	—	—	300	300
	H ₂ O g/m ³	100	100	100	100	—
T4CDD		548	351	427	315	63
F5CDD		797	612	848	700	226
H6CDD		462	752	973	820	785
H7CDD		138	335	320	367	1529
OCDD		17	49	70	94	1288
PCDD		1962	2299	2638	2296	3891
T4CDF		904	1075	1180	935	718
P5CDF		806	1206	1188	1087	1050
H5CDF		349	695	730	780	1626
H7CDF		53	150	122	183	1381
OCDF		0	20	28	45	1361
PCDF		2112	3146	3248	3030	6136

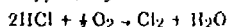
Table 2: Effect of SO₂/HCl on the Formation of PCDD/PCDF on Fly Ash with 4% Active Charcoal. Temperature 300 °C, 2 hrs.

Gasphase	SO ₂ mg/m ³	—	300	600	300	600	900	300	300
	HCl mg/m ³	—	—	—	—	—	—	300	300
	H ₂ O g/m ³	100	100	100	—	—	—	100	—
T4CDD		69	115	20	7.5	0.8	0	245	44
F5CDD		68	127	12	18	1.8	0	279	107
H6CDD		32	78	2	73	10	7.3	182	186
H7CDD		17	22	1	107	32	19	55	191
OCDD		0	0	0	41	22	4	39	103
PCDD		206	342	35	246.5	66.6	30.3	800	631
T4CDF		992	772	226	317	43	28	1527	759
P5CDF		607	621	102	269	64	43	978	686
H5CDF		242	216	10	359	74	39	373	582
H7CDF		30	32	2	290	71	54	51	370
OCDF		0	0	0	502	231	31	0	443
PCDF		1871	1641	340	1737	483	195	2929	2840

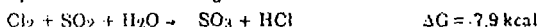
increase to 600 mg/m³ SO₂ the sums of PCDD and PCDF remain practically unchanged, as well as the pattern of the congener groups. The additional presence of 300 mg/m³ HCl leads to similar PCDD/PCDF concentrations, also with the preference of lower chlorinated species. The influence of water on dechlorination was reported earlier [5]. In the absence of water vapor and in the presence of

300 mg/m³ SO₂/HCl/H7CDD/OCDD and H6CDF to OCDF are the major components. The results from the annealing experiments of system B (carbon-free fly ash, with addition of 4% active charcoal) are given in table 2. No substantial effect is noted upon addition of 300 mg/m³ SO₂ in moist atmosphere, upon a further increase to 600 mg/m³ a decrease of PCDD/PCDF concentrations is noted. In dry systems with SO₂ concentrations of 600 and 900 mg/m³ marked decrease of PCDD/PCDF formation is noted.

Generally for the PCDD/PCDF synthesis on fly ash a mechanism is discussed which implies the in-situ-formation of chlorine via a Deacon reaction with chlorination of aromatics. The presence of SO₂ should inhibit these reactions as postulated by Griffin [4]. Our data are no direct support of this hypothesis. In the system with genuine fly ash (A) no decrease is noted, the PCDD/PCDF production is not influenced by SO₂ concentrations of up to 600 mg/m³. Apparently the reaction



with subsequent chlorination of organics and the removal of in-situ formed chlorine by



plays no major role in the PCDD/PCDF formation process.

Even the addition of gaseous HCl has no significant effect. Apparently the chloride of the fly ash is the more important reaction partner. On the other hand the system B with modified fly ash responds more sensitively. Here the SO₂ concentration (600 mg/m³) show an effect especially in the absence of water vapor. Also in moist atmospheres and with 600 mg/m³ of SO₂ a decrease of PCDD/PCDF by a factor of 10 and 5 respectively is obtained. In our interpretation the composition of the fly ash is a major factor controlling the PCDD/PCDF production. The difference of the behaviour of system B compared with genuine fly ash indicates that by the thermal pretreatment of fly ash (500° C) to remove organic carbon also the inorganic composition was changed. From the absence of any effect of SO₂ addition with genuine fly ash we conclude that intermediate formation of gaseous chlorine is not essential for chlorination reactions. The data support a mechanism mentioned previously [3] involving the following steps: a) interaction of the aromatic macrostructures of particulate carbon with Cu²⁺ and formation of organic radicals, b) direct reaction of these radicals with chloride and water to organic hydroxy- and chlorocompounds, c) oxidative degradation of these macro structures and formation of smaller, thermodynamically stable molecules, including CO₂. The effect observed in our experiments, especially in dry atmosphere with increasing SO₂ concentrations, can be explained by a general change of the redox potential of the fly ash, possibly by a shift of the Cu²⁺ = Cu⁺ equilibrium. Literature data from organic chemistry are additionally presented in favor of this hypothesis.

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